CLAIMS:

1. An electrostatic ion trap for a mass spectrometer, comprising:

an electrode arrangement defining an ion trapping volume;

the electrode arrangement being arranged to generate a trapping field defined by a potential $U'(r,\varphi,z)=U(r,\varphi,z)+W$, where $U(r,\varphi,z)$ is an ideal potential which traps ions in the Z-direction of the trapping volume so that they undergo substantially isochronous oscillations and where W is a perturbation to that ideal potential $U(r,\varphi,z)$;

wherein:

the geometry of the electrode arrangement generally follows one or more lines of equipotential of the ideal potential $U(r,\varphi,z)$ but wherein at least a part of the electrode arrangement deviates to a degree from that ideal potential $U(r,\varphi,z)$ so as to introduce the perturbation W into the said trapping field, the degree of deviation from the ideal potential $U(r,\varphi,z)$ being sufficient to result in the relative phases of the ions in the trap shifting over time such that at least some of the trapped ions have an absolute phase spread of more than zero but less than about 2π radians over an ion detection period T_m.

2. The trap of claim 1, wherein the electrode arrangement is of a shape that produces a trapping field that traps ions such that, in a longitudinal direction z of the trap, they describe oscillations in which the period of oscillation depends upon the amplitude of oscillation.

3. The trap of claim 1 or claim 2, wherein the electrode arrangement is of a shape that produces a trapping field that traps ions such that, in a longitudinal direction z of the trap, they describe perturbed simple harmonic oscillations in which the period of oscillation depends upon the amplitude of oscillation.

4. The trap of claim 2 or claim 3, wherein the average rate of change of period as a function of amplitude A_z, $\frac{d\tau}{dA_z}$, is positive such that an increasing amplitude of oscillation causes an increase in ion oscillation period.

5. The trap of any preceding claim, wherein the shape of at least a part of the electrode arrangement deviates from the ideal equipotential by an amount sufficient to impart an n^{th} order perturbation to the ideal potential $U(r,\varphi,z)$, where $n\geq 2$.

6. The trap of claim 5, wherein the deviation of the shape of at least a part of the electrode arrangement deviates from the ideal potential $U(r,\varphi,z)$ by an amount sufficient to introduce a negative, fourth order term into the ideal expression $U(r,\varphi,z)$.

7. The trap of any preceding claim, wherein the electrode arrangement comprises first and second electrode structures defining between them the said ion trapping volume.

8. The trap of claim 7, wherein the first electrode structure comprises a radially inner electrode extending in the z-direction and having a maximum diameter D1, and the

second electrode structure comprises a radially outer electrode also extending in that z-direction and having a maximum diameter D2, the trapping field being arranged to trap ions in an potential well along the z direction and also radially. .

9. The trap of claim 8, wherein the inner and outer electrodes conform to a shape defined by an equipotential of a trapping field of the form $U'(r,\varphi,z)$, where $U'(r,\varphi,z)=U(r,\varphi,z)+W$, $U(r,\varphi,z)$ defines an ideal electrostatic field in which

$$U(r,\varphi,z) = \frac{k}{2}\left[z^2 - \frac{r^2}{2}\right] + \frac{K}{2}(R_M)^2 \bullet \ln\left[\frac{r}{R_m}\right]$$

where: $U(r,\varphi,z)$ is the potential at a point r,φ,z in cylindrical coordinates within the trap;

k is the field curvature; and

$R_m>0$ is the characteristic radius

and where W is a field perturbation dependent upon at least z and which results in the ion oscillation period, T, in the Z-direction, depending upon the ion oscillation amplitude A, which in turn causes the net phase shift of ions to be greater than zero but less than about 2πradians over the said ion detection time T_m.

10. The trap of claim 8or claim 9, wherein the outer electrode is stretched or shifted in the z-direction relative to the ideal equipotential of $U(r,\varphi,z)$.

11. The trap of claim 10, wherein the amount of stretch of the outer electrode is no more than $(1\text{x}10^{-3})$D2, and preferably less than 0.0003D2.

12. The trap of claim 8, 9, 10 or 11, wherein the inner electrode has a maximum diameter D1 at z=0 which is smaller than the maximum of r at Z=0 defined by the ideal equipotential of $U(r,\varphi,z)$.

13. The trap of claim 12, wherein the maximum diameter D1 in the z-direction is about 0.03 to 0.07% smaller than it would be at z=0 if it conformed to an equipotential of the ideal expression $U(r,\varphi,z)$.

14. The trap of any of claims 8 to 13, wherein the outer electrode has a maximum inner diameter D2 at z=0 which is larger than the maximum of r at z=0 defined by the ideal equipotential of $U(r,\varphi,z)$.

15. The trap of claim 14, wherein the maximum diameter D2 is about 0.02% larger than it would be at z=0 if it conformed to an equipotential of the ideal expression $U(r,\varphi,z)$.

16. The trap of any of claims 8 to 15, wherein the outer electrode comprises first and second axially spaced segments.

17. The trap of claim 16, further comprising a spacer mounted between the first and second axially spaced segments of the outer electrode.

18. The trap of claim 16 or claim 17, wherein the first and second axially spaced segments are dislocated outwards by no more than 0.5% of D2, and optionally no more than 0.1% thereof.

19. The trap of any of claims 7 to 18, wherein the outer electrode comprises a plurality of axially spaced segments.

20. The trap of claim 19, wherein the outer electrode comprises first and second axially spaced, relatively inward segments, sandwiched between third and fourth axially spaced, relatively outward segments.

21. The trap of any of claims 1 to 20, further comprising detection means for detecting ions in the trap.

22. The trap of claim 21 when dependent upon claim 20, wherein the detection means includes two of the first, second, third and fourth axially spaced segments.

23. The trap of claim 22, wherein the detection means further includes a differential detector, connected so as to determine the difference between the outputs from the said two of the segments which form a part of the detection means.

24. The trap of any one of claims 8 to 23, wherein the parameters of the trap conform to at least one of the criteria selected from the list comprising:

(a) the inner diameter at the axial location z=0 of the outer electrode, D2, lies within the range 20 mm<D2<50 mm and optionally between 25 and 35 mm;

(b) the outer diameter at the axial location z=0 of the inner electrode D1 is <0.8D2 and optionally between 0.3D2 and 0.5D2;

(c) the parameter R_m lies in the range $0.5D2<R_m<2D2$ and optionally between 0.55D2 and 0.95D2;

(d) the axial length of the trap is greater than 2(D2-D1) and preferably greater than 1.4D2;

(e) the inner and outer electrodes conform to the said hyper-logarithmic form to an accuracy better than $(5x10^{-4})$D2, optionally better than $(5x10^{-5})$D2;

(f) the degree of tilt of the central electrode is less than 1% of D2, optionally <0.1% thereof;

(g) the misalignment of the outer electrodes is <0.3% of D2), optionally <0.03% thereof;

(h) the systematic mismatch between outer electrodes is <0.1% of D2, optionally <0.005% thereof;

(i) the surface finish is better than $2x10^{-4}$D2, preferably better than $3x10^{-5}$D2.

25. The trap of any of claims 8 to 24, further comprising an entrance slot formed in the radially outer electrode to allow injection of ions into the trap; wherein the entrance slot has a width, in the z direction, less than 0.07D2 and preferably between 0.02D2 and 0.03D2, and a length (in a direction perpendicular to the direction Z) less than 0.2D2, and preferably between 0.12D2 and 0.16D2 in that direction.

26. An electrostatic ion trap for a mass spectrometer as claimed in any one of the preceding claims, further comprising field perturbation means arranged to introduce the perturbation W to the ideal potential $U(r,\varphi,z)$ so as to enforce a relative shift in the phases of the ions over time such that at least some of the trapped ions have an absolute phase spread of more than zero but less than about 2π radians over an ion detection period T_m.

27. An electrostatic ion trap for a mass spectrometer comprising:

an electrode arrangement defining an ion trapping volume;

the electrode arrangement being arranged to generate a trapping field defined by a potential $U(r,\varphi,z)$ where $U(r,\varphi,z)$ is a potential which traps ions in the Z-direction of the trapping volume so that they undergo substantially isochronous oscillations;

wherein the trap further comprises field perturbation means to introduce a perturbation W to the potential $U(r,\varphi,z)$ so as to enforce a relative shift in the phases of the ions over time such that at least some of the trapped ions have an absolute phase spread of more than zero but less than about 2π radians over an ion detection period T_m.

28. The trap of claim 27, wherein the field perturbation means comprises a magnet for providing a mass dependent correction to the electrostatic field perturbation W.

29. The trap of claim 27or claim 28, wherein the outer electrode comprises first and second axially spaced segments.

30. The trap of claim 29, further comprising a spacer mounted between the first and second axially spaced segments of the outer electrode.

31. The trap of claim 29 or 30, wherein the first and second axially spaced segments are separated by no more than 0.5% of D2, and optionally no more than 0.1% thereof.

32. The trap of any of claims 27 to 31, wherein the outer electrode comprises a plurality of axially spaced segments.

33. The trap of claim 32, wherein the outer electrode comprises first and second axially spaced, relatively inward segments, sandwiched between third and fourth axially spaced, relatively outward segments.

34. The trap of any of claims 27 to 33, further comprising detection means for detecting ions in the trap.

35. The trap of claim 34 when dependent upon claim 33, wherein the detection means includes two of the first, second, third and fourth axially spaced segments.

36. The trap of claim 35, wherein the detection means further includes a differential detector, connected so as to determine the difference between the outputs from the said two of the segments which form a part of the detection means.

37. The trap of any of claims 27 to 36, wherein the field perturbation means includes a power supply arranged to supply a perturbation voltage to at least one of the electrodes so as to introduce the said perturbation W to the ideal field $U(r,\varphi,z)$.

38. The trap of any of claims 27 to 36, the field perturbation means comprising one or more trap end caps to which a perturbation voltage is applied.

39. A method of trapping ions in an electrostatic trap having an electrode assembly, comprising:

applying a substantially electrostatic trapping potential to at least a part of the electrode assembly, so as to generate an electrostatic trapping field within the trap, for trapping ions of a mass to charge ratio m/q in a volume V such that they undergo multiple isochronous reflections along a longitudinal axis of the trap; and

distorting the geometry of the trap, and/or distorting at least a part of the trapping potential, and/or applying an additional distortion potential to one or more parts of the electrode assembly;

so as to cause a perturbation in the electrostatic trapping field which results in at least some of the ions of mass to charge ratio m/q to undergo a separation in phase of no more than 2π radians over a measurement time period T_m.

40. The method of claim 39, further comprising distorting the geometry of the trap, and/or distorting at least a part of the trapping potential, and/or applying an additional distortion potential to one or more parts of the electrode assembly to an extent such that the average rate of change of period as a function of amplitude A_z, $\frac{d\tau}{dA_z}$, is positive such that an increasing amplitude of oscillation causes an increase in ion oscillation period.

41. The method of claim 39 or claim 40, wherein the perturbed trapping field is of the form

$U'(r,\varphi,z)=U(r,\varphi,z)+W$, where $U(r,\varphi,z)$ is an ideal trapping potential and W is a distortion thereto, and wherein the step of distorting the geometry of the trap comprises distorting the shape of at least a part of the electrode arrangement such that it deviates from an equipotential of the ideal potential $U(r,\varphi,z)$ by an amount sufficient to impart an n^{th} order perturbation to the ideal potential $U(r,\varphi,z)$, where $n\geq 2$.

42. The trap of claim 41, wherein the step of distorting the geometry of the trap comprises distorting the shape of at least a part of the electrode arrangement such that it deviates from the said equipotential of the ideal potential $U(r,\varphi,z)$ by an amount sufficient to introduce a negative, fourth order term into the ideal expression $U(r,\varphi,z)$.

43. The method of claim 39, wherein the trap comprises a plurality of trapping electrodes to generate the electrostatic trapping field and at least one distortion electrode, the method further comprising applying a voltage to the distortion electrode to add a perturbation to the electrostatic trapping field so as to create at least a part of the said perturbation in the trapping field.

44. The method of claim 39, wherein the electrostatic trap comprises first and second electrode structures defining therebetween the said trapping volume V and each generally following a line of equipotential of an ideal trapping field, the step of applying a distortion to the geometry of the trap comprising stretching or shifting one or both of the first and second electrode structures relative to the ideal trapping field equipotential so as to

introduce the said geometric distortion that results in the said ion phase separation.

45. A method of construction of an electrostatic ion trap comprising an electrode assembly arranged to generate a trapping field for trapping ions of mass to charge ratio m/q within the trap, the method comprising the steps of:

manufacturing one or more components of the electrode assembly to within a stipulated tolerance of a nominal shape and/or dimension;

measuring at least one parameter of the manufactured component(s) to a precision greater than the stipulated tolerance;

selecting those components of the electrode assembly whose measured parameter(s) are found to differ from the nominal shape and/or dimension by an amount that results in the addition, to the trapping field, of a perturbation W which causes at least some of the ions of mass to charge ratio m/q to undergo a separation in phase of no more than 2π radians over a measurement time period T_m; and

constructing a trap from the selected components.

46. The method of claim 45, further comprising

determining a performance parameter of the constructed trap.

47. The method of claim 46, wherein the step of determining a performance parameter of the trap comprises:

supplying a plurality of ions to the constructed trap;

detecting at least some of the ions in the trap; and

generating data which is directly or indirectly representative of the mass to charge ratio of the detected ions.

48. The method of claim 47, further comprising:
obtaining a mass spectrum from the generated data;
ascertaining whether or not the peaks in the obtained mass spectrum are split; and
rejecting the constructed trap when split peaks are detected.

49. The method of claim 47, further comprising
obtaining a mass spectrum from the generated data;
determining the relative abundances of isotopes of a known ion in the mass spectrum; and
rejecting the trap when the degree to which these relative abundances correspond with predicted (theoretical or naturally occurring) abundances exceed a threshold level.

50. The method of claim 47, wherein the step of generating data which is directly or indirectly representative of the mass to charge ratio of ions in the trap comprises generating a time domain transient from the ions in the trap, the transient containing information on those ions;
the step of determining a performance parameter of the trap further comprising determining the decay of the transient over an ion detection time T_m;
the method further comprising rejecting a trap wherein the said transient decays from a maximum amplitude to below a predetermined threshold level in the said ion detection time T_m.

51. The method of claim 50, wherein the predetermined threshold level is selected from the list comprising 50%, 30%, 10%, 5% and 1% of the maximum amplitude.

52. The method of claim 47, further comprising:

supplying a plurality of ions to the constructed trap at a first ion injection energy;

detecting at least some of the ions injected into the trap with that first ion injection energy and producing a first data set representative of a parameter of those detected ions;

obtaining a first mass spectrum from the thus generated first data set;

supplying a plurality of ions to the constructed trap at a second ion injection energy;

detecting at least some of the ions injected into the trap with that second ion injection energy and producing a second data set representative of a parameter of those detected ions;

obtaining a second mass spectrum from the thus generated second data set;

comparing at least a part of the first and second mass spectra to ascertain whether there is a dependence of detected mass upon the said ion injection energy; and

rejecting the constructed trap when it is determined that there is a dependence of detected mass upon ion injection energy and which exceeds a threshold criterion.

53. The method of any of claims 45 to 52, wherein the step of selecting measured components comprises selecting components whose measured shape and/or dimensions are complementary so that the net distortion of the electrodes is such as to introduce a perturbation of the desired magnitude.